

Walsh's method and ours are both indirect, each with assumptions that are reasonable but not infallible. Consequently, while the agreement over  $\beta$ -stabilization is pleasing, the extent of  $\alpha$ -stabilization remains an open question. From ESR studies on  $\cdot\text{CH}_2\text{SiMe}_3$  radicals generated by hydrogen abstraction, Krusic and Kochi<sup>10</sup> concluded that these radicals might be more stable than their alkyl counterpart. Although their explanation of the nature of that stabilization has been challenged,<sup>11</sup> it remains an experimental fact that radicals could be generated from  $\text{Me}_4\text{Si}$  but not from  $\text{Me}_4\text{C}$  under the same conditions. Similar enhanced reactivity in analogous circumstances was observed by Sakurai and co-workers.<sup>12</sup> Likewise, Wilt and co-workers found that  $\alpha$ -halosilanes were more reactive than haloalkanes in free radical reduction by organotin hydrides; stabilization of the transition state for halogen abstraction by a polar effect was the preferred explanation,<sup>13</sup> but  $\alpha$ -silyl radical stabilization could have been a contributory factor. Ingold and his co-authors<sup>14</sup> found enhanced reactivity toward hydrogen abstraction at both the  $\alpha$ - and  $\beta$ -carbons of  $\text{Et}_4\text{Si}$ ; they considered the  $\beta$ -stabilization effect to be greater than the

$\alpha$ -effect, but comparisons are complicated by uncertainty over the allowance that should be made for steric hindrance when  $\text{Et}_4\text{Si}$  was compared with hydrocarbon prototypes. Walsh<sup>15</sup> has suggested that some of the " $\alpha$ -stabilization" we observed with compound VI may simply result from release of gauche interactions, but these are believed<sup>16</sup> to be small in organosilanes because bonds to silicon are long. We undertook some measurements with Chemgraf<sup>17</sup> that were consistent with that. We found in these measurements that the difference in energy between gauche and trans conformations in *n*-propyltrimethylsilane was 4 times smaller than that in VIII. As the gauche interaction in the latter is 0.8 kcal,<sup>18</sup> the two gauche interactions in VI would total only 0.4 kcal.

Clearly, both the  $\alpha$ - and  $\beta$ -silyl stabilization effects are small and elusive, but our results indicate that they may be closer in magnitude to each other than has been supposed hitherto.

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(9) Doncaster, A. M.; Walsh, R. *J. Chem. Soc., Faraday Trans. 1* 1976, 72, 2908.

(10) Krusic, P. J.; Kochi, J. K. *J. Am. Chem. Soc.* 1969, 91, 6161.

(11) Lyons, A. R.; Neilson, G. W.; Symons, M. C. R. *J. Chem. Soc., Faraday Trans. 2* 1972, 68, 807.

(12) Sakurai, H.; Hosomi, A.; Kumada, M. *Bull. Chem. Soc. Jpn.* 1971, 44, 568.

(13) Wilt, J. W.; Belmonte, F. G.; Zieske, P. A. *J. Am. Chem. Soc.* 1983, 105, 5665.

(14) Jackson, R. A.; Ingold, K. U.; Griller, D.; Nazran, A. S. *J. Am. Chem. Soc.* 1985, 107, 208.

(15) Walsh, R., personal communication.

(16) O'Neal, H. E.; Ring, M. A. *J. Organomet. Chem.* 1981, 213, 419.

(17) Chemgraf, created by E. K. Davies, Chemical Crystallography Laboratory, Oxford University, developed and distributed by Chemical Design Ltd., Oxford.

(18) Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; Wiley: New York, 1976.

## Kinetics of Pyrolysis of Some Alkenylsilanes

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Kinetic measurements and product analyses are described for the pyrolysis of four alkenylsilanes: 4-dimethylsilyl-1-butene (I), 4-(trimethylsilyl)-1-butene (II), 5-(dimethylsilyl)-1-pentene (III), and 5-(trimethylsilyl)-1-pentene (IV). Retroene reactions and secondary radical reactions leading to the observed products are discussed.

### Introduction

Our gas-kinetic studies of the pyrolysis of allyltrimethylsilane<sup>1,2</sup> have shown that there are two concurrent primary reactions, homolysis of the silicon-allyl bond to form radicals and retroene elimination of dimethylsilene, and that one of the major products, trimethylvinylsilane, is formed by a secondary radical addition reaction rather than by the unimolecular sequences previously suggested.<sup>3,4</sup> The two concurrent primary reactions were distinguished from each other by pyrolysis with excess methyl chloride, which acted as a selective trap for trimethylsilyl radicals, thus enabling Arrhenius parameters for the homolysis to

be deduced from the kinetics of formation of trimethylchlorosilane.

We have subsequently applied the same methods to four higher alkenylsilanes: 4-(dimethylsilyl)-1-butene (I), 4-(trimethylsilyl)-1-butene (II), 5-(dimethylsilyl)-1-pentene (III), and 5-(trimethylsilyl)-1-pentene (IV). Trapping with methyl chloride enabled some conclusions to be drawn about the effect of  $\alpha$ - and  $\beta$ -silyl substitution on the stability of the alkyl radicals formed by homolysis of the allyl-carbon bonds in I-IV.<sup>5</sup> In the case of I, it was also possible to investigate quantitatively the radical isomerization reaction (1).<sup>6</sup> As in the pyrolysis of allyltri-



methylsilane, these radical-forming primary homolyses

(1) Davidson, I. M. T.; Wood, I. T. *J. Organomet. Chem.* 1980, 187, C65.

(2) Barton, T. J.; Burns, S. A.; Davidson, I. M. T.; Ijadi-Maghsoodi, S.; Wood, I. T. *J. Am. Chem. Soc.* 1984, 106, 6367.

(3) Sakurai, H.; Hosomi, A.; Kumada, M. *J. Chem. Soc., Chem. Commun.* 1970, 767.

(4) Neider, S. M.; Chambers, G. R.; Jones, M., Jr. *Tetrahedron Lett.* 1979, 40, 3793.

(5) Davidson, I. M. T.; Barton, T. J.; Hughes, K. J.; Ijadi-Maghsoodi, S.; Revis, A.; Paul, G. C. *Organometallics*, second of three papers in this issue.

(6) Barton, T. J.; Revis, A.; Davidson, I. M. T.; Ijadi-Maghsoodi, S.; Hughes, K. J.; Gordon, M. S. *J. Am. Chem. Soc.* 1986, 108, 4022.

Table I. Kinetic Results by LPP with Excess MeCl<sup>c</sup>

compd	formation of Me <sub>3</sub> SiCl			total decomposition			temp/°C
	log A/s <sup>-1</sup>	E/kcal	k <sub>570°C</sub>	log A/s <sup>-1</sup>	E/kcal	k <sub>570°C</sub>	
I	15.5 ± 0.4	68.4 ± 2	5.8 × 10 <sup>-3</sup>	12.8 ± 0.2	56.9 ± 1	1.1 × 10 <sup>-2</sup>	532-593
II	14.6 ± 0.4	68.6 ± 2	6.5 × 10 <sup>-4</sup>	12.1 ± 0.2	54.7 ± 2	8.3 × 10 <sup>-3</sup>	567-630
III	15.4 ± 0.4	67.6 ± 2	7.5 × 10 <sup>-3</sup>	11.5 ± 0.2	49.7 ± 1	4.1 × 10 <sup>-2</sup>	500-575
IV	15.3 ± 0.5	67.4 ± 2	6.7 × 10 <sup>-3</sup>	11.8 ± 0.2	50.7 ± 1	4.5 × 10 <sup>-2</sup>	510-579
	[15.6 ± 0.5]	73.0 ± 2	4.7 × 10 <sup>-4</sup>	12.9 ± 0.1	59.5 ± 5	3.0 × 10 <sup>-3</sup>	590-670) <sup>b</sup>

<sup>a</sup> With III, the chlorosilane product was HMe<sub>2</sub>SiCl, not Me<sub>3</sub>SiCl. <sup>b</sup> Corresponding data for allyltrimethylsilane.

were accompanied by interesting secondary radical reactions and by retroene eliminations. This paper deals with those aspects of the pyrolysis of I-IV.

### Results

The pyrolysis of each compound I-IV was studied by two complementary techniques, low-pressure pyrolysis with analysis by quadrupole mass spectrometry (LPP)<sup>7</sup> and batch stirred flow in a carrier gas of dried deoxygenated nitrogen at ca. 1000 torr with analysis by gas chromatography (SFR).<sup>8</sup> Most products were identified by comparison with authentic samples and verified for every product by GC/mass spectrometry in a static pyrolysis system.

In the SFR experiments, initial partial pressures of each silane were 0.08-0.8 torr. Initial pressures in LPP experiments were 0.02-0.05 torr. When methyl chloride was added in LPP experiments, it was in 9-fold excess, giving initial silane partial pressures of 0.002-0.005 torr. Reactions were found to be first order within these ranges of initial pressure.

In each case it proved to be more difficult to suppress secondary reactions than it was in the pyrolysis of allyltrimethylsilane.<sup>2</sup> The conditions least favorable to bimolecular secondary reactions being the LPP experiments with excess methyl chloride, where the partial pressures of silane were lowest, the first-order Arrhenius parameters in Table I were closer to being measures of primary reactions than kinetic data obtained in SFR experiments. The mass spectrometric peaks monitored to produce the results in Table I were chosen to give the best balance between intensity and small contributions from interfering peaks: the molecule - ion M<sup>+</sup> for formation of Me<sub>3</sub>SiCl from I and II, (M - 15)<sup>+</sup> for the corresponding process for III and IV, (M - 28)<sup>+</sup>, (M - 15)<sup>+</sup> and (M - 41)<sup>+</sup> for decomposition of I, II, and both III and IV, respectively. Although the SFR experiments did not provide as useful kinetic data as LPP, they were a valuable source of information on product composition. Once products had been identified by GC/mass spectrometry, their relative yields were measured in the SFR. The results in Table II were obtained in pyrolyses in the SFR at various temperatures, with no added methyl chloride. The inequalities in Table II reflect difficulties in resolving GC peaks. The effect of added methyl chloride on the product composition was also studied in the SFR. In the pyrolysis of I, added methyl chloride increased the production of methane (2×) and C<sub>4</sub>H<sub>8</sub>, mainly 1-butene (4×) with a smaller increase in butadiene formation. There was decreased formation of dimethylvinylsilane (2×), trimethylvinylsilane (4×), allyltrimethylsilane (5×), and allyldimethylsilane (7×). In the pyrolysis of II, the main changes were increased formation of methane (4×) and small increases in 1-butene and butadiene but decreased formation of trimethyl-

Table II. Product Composition from SFR Experiments<sup>a,b</sup>

compd	I [17.6] (587 °C)	II [18.2] (577 °C)	III [20.2] (580 °C)	IV [20.7] (600 °C)
CH <sub>4</sub> [1.0] <sup>c</sup>	~1	6	~1	<1
C <sub>2</sub> H <sub>4</sub> [2.1] <sup>c</sup>	32	13	25	25
C <sub>3</sub> H <sub>6</sub> [8.2] <sup>c</sup>	13	11	32	33
C <sub>4</sub> H <sub>8</sub> [11.9] <sup>c</sup>	≤3	≥9	1	1
C <sub>4</sub> H <sub>8</sub> [11.7] <sup>c</sup>	≤1.5	≥11	1	1
Me <sub>2</sub> SiH <sub>2</sub> [10.8] <sup>c</sup>	3	3	3	<1
Me <sub>3</sub> SiH [12.5] <sup>c</sup>	≤19	≤3	1	3
Me <sub>4</sub> Si [13.5] <sup>c</sup>	1	≤15	<1	1
HMe <sub>2</sub> SiCH <sub>2</sub> CH <sub>2</sub> [14.2]	≥6		28	1
Me <sub>3</sub> SiCH <sub>2</sub> CH <sub>2</sub> [15.2]	1.5	11	~1	27
HMe <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> [15.9]	5		7	1
Me <sub>3</sub> SiCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> [16.7] <sup>c</sup>	10	15	~1	7
Me <sub>3</sub> SiCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> [18.2] <sup>c</sup>				<1
DSCB [~15] <sup>c</sup>	≤1.5	≤3	<1	<1
DMSP [~15] <sup>c,d</sup>	≤1.5			
DMSH [~37] <sup>c,d</sup>			~1	

<sup>a</sup> DSCB = 1,1,3,3-tetramethyl-1,3-disilacyclobutane. DMSP = 1,1-dimethylsilacyclopent-3-ene. DMSH = 1,1-dimethylsilacyclohex-3-ene. <sup>b</sup> Retention times (min) on the Chromosorb column in square brackets. <sup>c</sup> Retention time checked against authentic sample. <sup>d</sup> Retention time on the SE-30 column.

vinylsilane (3×) and allyltrimethylsilane (4×). In the pyrolysis of III, added methyl chloride had no effect on the formation of vinyltrimethylsilane but reduced allyldimethylsilane (4×). Similarly, in the pyrolysis of IV, trimethylvinylsilane was unaffected but allyltrimethylsilane was reduced (4×).

### Discussion

The results in Table I for the formation of trimethylchlorosilane have been discussed previously.<sup>5</sup> Allyl-carbon bond homolysis in the pyrolysis of I, III, and IV initiates unimolecular sequences leading to silyl radicals and hence to a chlorosilane, but in the case of II the trimethylsilyl radicals are formed in a bimolecular addition reaction that is only one of the possibilities open to the initially formed radical. Consequently, the Arrhenius parameters for the formation of trimethylchlorosilane from II certainly underestimate the homolysis pathway whereas the corresponding parameters for the other three compounds may be reasonable measures of homolysis. The latter is a faster process in I-IV than in allyltrimethylsilane mainly because the allyl-carbon bond in these compounds is weaker than allyl-silicon. The true Arrhenius parameters for homolysis in the pyrolysis of II are likely to be very similar to those of I. If so, the rate constant for total decomposition of II is ca. 43% greater than that for homolysis. As there is no reasonable retroene reaction for II, that difference is probably attributable to secondary reactions. On the other hand, the retroene reactions in Scheme I may be envisaged for compounds I, III, and IV. These reactions cause the rate constants for total decomposition to be greater than for II, but we cannot reliably calculate Arrhenius parameters for the retroene reactions as we did for allyltri-

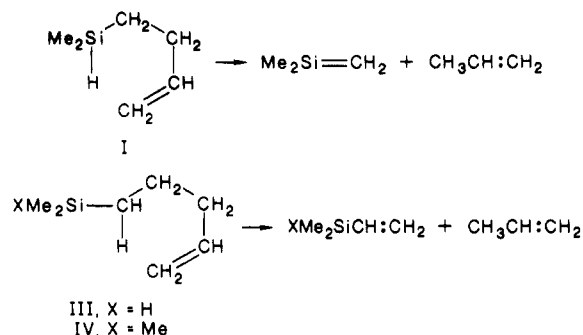
(7) Davidson, I. M. T.; Ring, M. A. *J. Chem. Soc., Faraday Trans. 1* 1980, 76, 1520.

(8) Baldwin, A. C.; Davidson, I. M. T.; Howard, A. V. *J. Chem. Soc., Faraday Trans. 1* 1975, 71, 972.

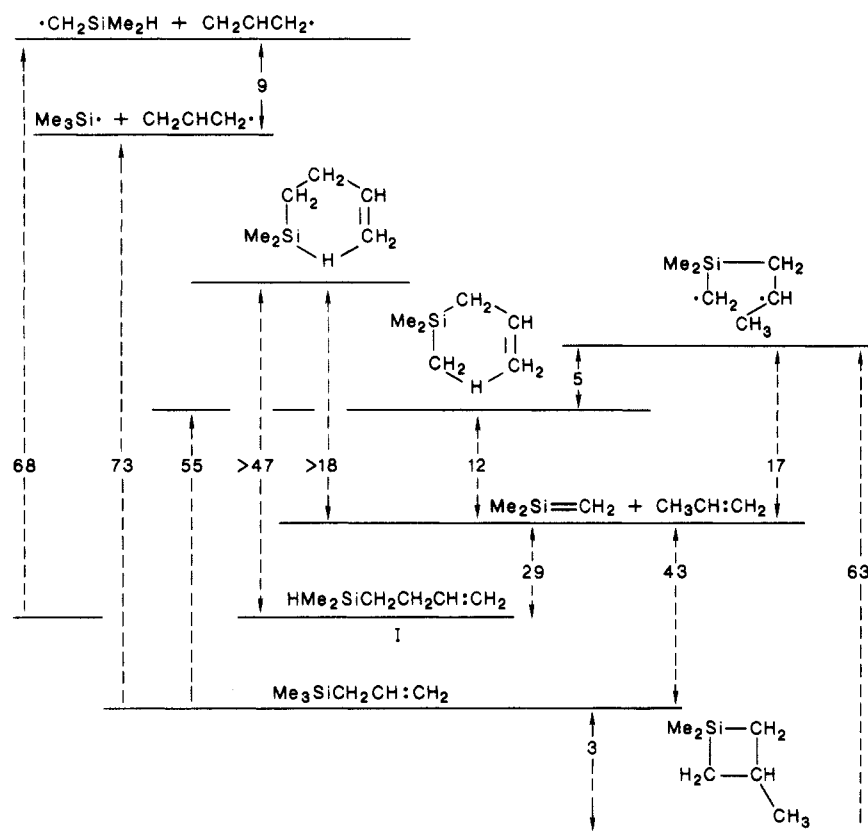
Table III. Products of Radical Addition Reactions

reactants		terminal addition		internal addition	
compd	radical	products	new radical	products	new radical
I	Me <sub>3</sub> Si <sup>•</sup>	Me <sub>3</sub> SiCH <sub>2</sub> CH:CH <sub>2</sub>	Me <sub>3</sub> Si <sup>•</sup>	Me <sub>3</sub> SiCH:CH <sub>2</sub> , C <sub>2</sub> H <sub>4</sub>	HMe <sub>2</sub> Si <sup>•</sup>
	HMe <sub>2</sub> Si <sup>•</sup>	HMe <sub>2</sub> SiCH <sub>2</sub> CH:CH <sub>2</sub>	Me <sub>3</sub> Si <sup>•</sup>	HMe <sub>2</sub> SiCH:CH <sub>2</sub> , C <sub>2</sub> H <sub>4</sub>	HMe <sub>2</sub> Si <sup>•</sup>
	Me <sup>•</sup>	CH <sub>3</sub> CH <sub>2</sub> CH:CH <sub>2</sub>	Me <sub>3</sub> Si <sup>•</sup>	CH <sub>3</sub> CH:CH <sub>2</sub> , C <sub>2</sub> H <sub>4</sub>	HMe <sub>2</sub> Si <sup>•</sup>
II	Me <sub>3</sub> SiCH <sub>2</sub> <sup>•</sup>	none (reversible reaction)		Me <sub>3</sub> SiCH <sub>2</sub> CH:CH <sub>2</sub> , C <sub>2</sub> H <sub>4</sub>	Me <sub>3</sub> Si <sup>•</sup>
	Me <sub>3</sub> Si <sup>•</sup>	Me <sub>3</sub> SiCH <sub>2</sub> CH:CH <sub>2</sub>	Me <sub>3</sub> SiCH <sub>2</sub> <sup>•</sup>	Me <sub>3</sub> SiCH:CH <sub>2</sub> , C <sub>2</sub> H <sub>4</sub>	Me <sub>3</sub> Si <sup>•</sup>
	Me <sup>•</sup>	CH <sub>3</sub> CH <sub>2</sub> CH:CH <sub>2</sub>	Me <sub>3</sub> SiCH <sub>2</sub> <sup>•</sup>	CH <sub>3</sub> CH:CH <sub>2</sub> , C <sub>2</sub> H <sub>4</sub>	Me <sub>3</sub> Si <sup>•</sup>
III	HMe <sub>2</sub> Si <sup>•</sup>	HMe <sub>2</sub> SiCH <sub>2</sub> CH:CH <sub>2</sub> , C <sub>2</sub> H <sub>4</sub>	HMe <sub>2</sub> Si <sup>•</sup>	HMe <sub>2</sub> SiCH:CH <sub>2</sub> , C <sub>2</sub> H <sub>4</sub>	Me <sub>3</sub> Si <sup>•</sup>
	Me <sub>3</sub> Si <sup>•</sup>	Me <sub>3</sub> SiCH <sub>2</sub> CH:CH <sub>2</sub> , C <sub>2</sub> H <sub>4</sub>	HMe <sub>2</sub> Si <sup>•</sup>	Me <sub>3</sub> SiCH:CH <sub>2</sub> , C <sub>2</sub> H <sub>4</sub>	Me <sub>3</sub> Si <sup>•</sup>
	Me <sup>•</sup>	CH <sub>3</sub> CH <sub>2</sub> CH:CH <sub>2</sub> , C <sub>2</sub> H <sub>4</sub>	HMe <sub>2</sub> Si <sup>•</sup>	CH <sub>3</sub> CH:CH <sub>2</sub> , C <sub>2</sub> H <sub>4</sub>	Me <sub>3</sub> Si <sup>•</sup>
IV	Me <sub>3</sub> Si <sup>•</sup>	Me <sub>3</sub> SiCH <sub>2</sub> CH:CH <sub>2</sub> , C <sub>2</sub> H <sub>4</sub>	Me <sub>3</sub> Si <sup>•</sup>	Me <sub>3</sub> SiCH:CH <sub>2</sub> , C <sub>2</sub> H <sub>4</sub>	Me <sub>3</sub> SiCH <sub>2</sub> <sup>•</sup>
	Me <sub>3</sub> SiCH <sub>2</sub> <sup>•</sup>	Me <sub>3</sub> SiCH <sub>2</sub> CH <sub>2</sub> CH:CH <sub>2</sub> , C <sub>2</sub> H <sub>4</sub>	Me <sub>3</sub> Si <sup>•</sup>	Me <sub>3</sub> SiCH <sub>2</sub> CH:CH <sub>2</sub> , C <sub>2</sub> H <sub>4</sub>	Me <sub>3</sub> SiCH <sub>2</sub> <sup>•</sup>
	Me <sup>•</sup>	CH <sub>3</sub> CH <sub>2</sub> CH:CH <sub>2</sub> , C <sub>2</sub> H <sub>4</sub>	Me <sub>3</sub> Si <sup>•</sup>	CH <sub>3</sub> CH:CH <sub>2</sub> , C <sub>2</sub> H <sub>4</sub>	Me <sub>3</sub> SiCH <sub>2</sub> <sup>•</sup>

Scheme I. Retroene Reactions of Compounds I, III, and IV



methylsilane<sup>2</sup> because of the evidence from the pyrolysis of II that bimolecular secondary radical reactions of these higher alkenylsilanes were not totally suppressed under our experimental conditions. Thus, in the case of I, subtraction of the rate constants for formation of trimethylchlorosilane from the rate constants for total decomposition over the temperature range of 532–593 °C gave residual Arrhenius parameters of  $\log A \approx 10.1$  and  $E \approx 47.9$  kcal·mol<sup>-1</sup>, but these are probably underestimates of the Arrhenius parameters and overestimates of the rate constant for the retroene reaction because of a contribution to the total rate constant from secondary radical reactions. In fact, Arrhenius parameters for the retroene formation

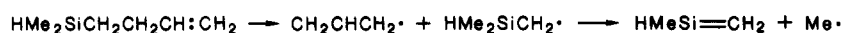
Scheme II. Energy Diagram for Allyltrimethylsilane and Compound I<sup>a</sup>

Scheme III. Thermochemistry of Retroene Reactions

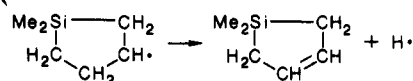
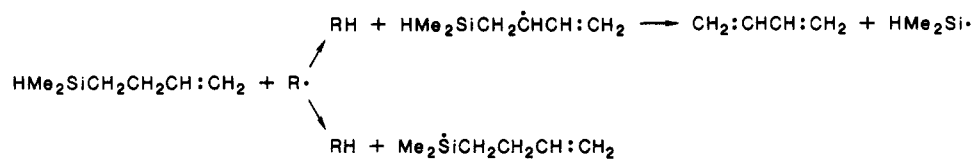
	$\Delta H/\text{kcal}$		$\Delta H/\text{kcal}$
Me <sub>3</sub> SiC <sub>3</sub> H <sub>5</sub> → Me <sub>3</sub> Si <sup>•</sup> + C <sub>3</sub> H <sub>5</sub> <sup>•</sup>	73	HMe <sub>2</sub> SiCH <sub>2</sub> C <sub>3</sub> H <sub>5</sub> → <sup>•</sup> CH <sub>2</sub> SiMe <sub>2</sub> H + C <sub>3</sub> H <sub>5</sub> <sup>•</sup>	68
Me <sub>3</sub> Si <sup>•</sup> → Me <sub>2</sub> Si=CH <sub>2</sub> + H <sup>•</sup>	99–40	<sup>•</sup> CH <sub>2</sub> SiMe <sub>2</sub> H → Me <sub>2</sub> Si=CH <sub>2</sub> + H <sup>•</sup>	90–40
H <sup>•</sup> + C <sub>3</sub> H <sub>5</sub> <sup>•</sup> → C <sub>3</sub> H <sub>6</sub>	-89	H <sup>•</sup> + C <sub>3</sub> H <sub>5</sub> <sup>•</sup> → C <sub>3</sub> H <sub>6</sub>	-89
	43		29

## Scheme IV. Radical Reactions in the Pyrolysis of Compound I

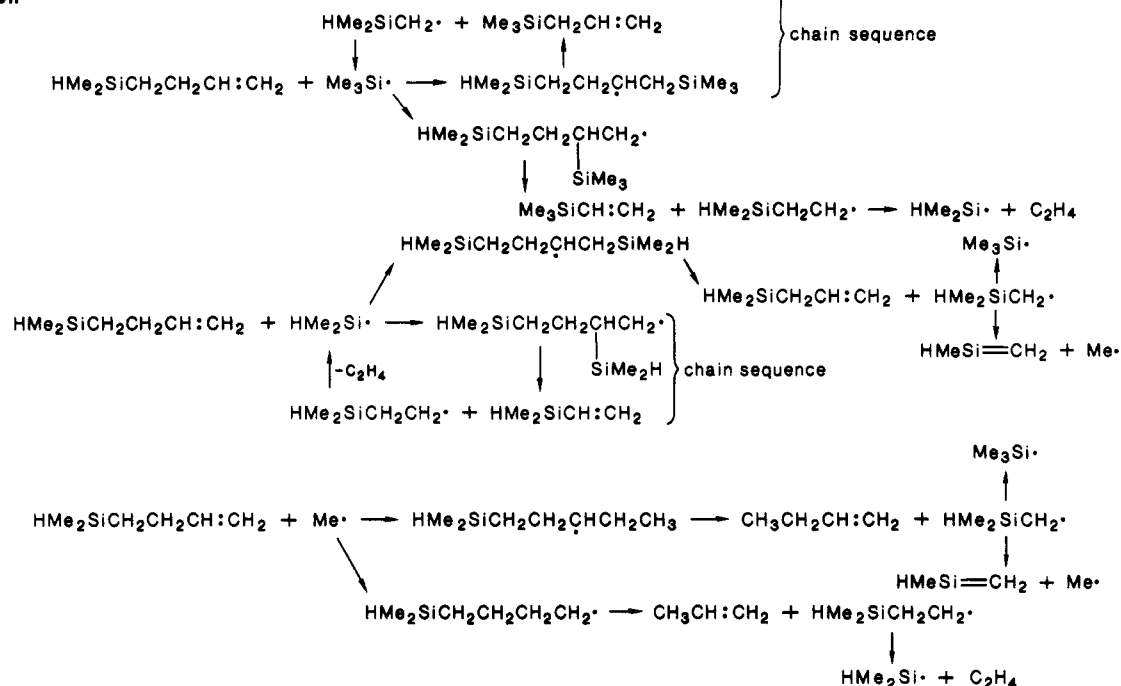
## Homolysis



## Abstraction



## Addition



of dimethylsilene and propene from I are more likely to be close to those for the very similar reaction of its isomer allyltrimethylsilane,<sup>2</sup> viz.,  $\log A = 11.6$  and  $E = 55$  kcal·mol<sup>-1</sup>, or of higher alkenes, e.g. 1-heptene.<sup>9</sup> On that basis, the energy diagram for reactions of allyltrimethylsilane<sup>2</sup> may be augmented to include reactions of its isomer I, as in Scheme II.  $\Delta H_1$  has been estimated previously.<sup>6</sup> Estimates of  $\Delta H$  for the retroene reactions of allyltrimethylsilane and I are from our kinetic measurements and published bond dissociation energies for silicon compounds<sup>10</sup> and hydrocarbons (Scheme III).<sup>11</sup>

It is obvious from the range of products in Table II that we are dealing with complex pyrolysis mechanisms, but some general conclusions are possible. As the analyses were done at different temperatures and as compounds I-IV different significantly in their thermal stability, we should focus our attention on the columns in Table II, not the rows.

Reasonable radical reactions in the pyrolysis of I are summarized in Scheme IV. Obvious abstraction products

such as  $\text{CH}_4$  from  $\text{Me}^\cdot$  and  $\text{Me}_3\text{SiH}$  from  $^\cdot\text{SiMe}_3$  are omitted for simplicity. Abstraction and addition reactions of the initially formed radical  $^\cdot\text{CH}_2\text{SiMe}_2\text{H}$  are also omitted. Reaction 1 is fast, with a half-life of ca. 1 ms at 570 °C; although it is reversible, the equilibrium has been shown to lie well to the right under the conditions used here.<sup>6</sup> DSCB, the product of dimerization of the dimethylsilene formed in the concurrent retroene reaction (Scheme I), was only a minor product (Table II) because silenes would mainly undergo addition to radicals, ultimately forming polymeric products. Both  $^\cdot\text{CH}_2\text{SiMe}_2\text{H}$  and  $^\cdot\text{SiMe}_3$  radicals can give methyl radicals by dissociation, but that process is also minor, as indicated by the small amount of methane. Formation of butadiene and DMSP suggests that abstraction reactions by any radical present occur both from the allylic carbon and from silicon; the radical resulting from the latter abstraction cyclizes in the endo fashion, as found by Barton and Revis<sup>12</sup> (because their experiments were done in solution, not at low pressure in the gas phase, the ultimate product was the silacyclopentane). Less butadiene and DMSP were formed than  $\text{Me}_3\text{SiH}$  partly because there would be some ab-

(9) Egger, K. W.; Vitins, P. *J. Am. Chem. Soc.* 1974, 96, 2714.

(10) Walsh, R. *Acc. Chem. Res.* 1981, 14, 246.

(11) Benson, S. W. *Thermochemical Kinetics*, 2nd ed., Wiley: New York, 1976.

(12) Barton, T. J.; Revis, A. *J. Am. Chem. Soc.* 1984, 106, 3802.

straction from other molecules besides I but mainly because the silicon-containing radicals produced by abstraction would undergo other secondary reactions. Radical addition reactions are important in these pyrolyses, as they were in the pyrolysis of allyltrimethylsilane,<sup>1,2</sup> but there are some quite subtle factors at play in determining the distribution of products from these reactions. This distribution depends not only on the balance between terminal and internal addition (terminal is favored), but also on whether a chain sequence can develop or not. As shown in Scheme IV, the latter factor could explain why there is more dimethylvinylsilane than trimethylvinylsilane, but more allyltrimethylsilane than allyldimethylsilane, in the pyrolysis of I. Application of similar arguments to the pyrolysis of II-IV leads to the conclusions in Table III, which summarizes the expected outcome of radical addition reactions.

Pyrolysis of II is simpler than I. Not only is there no retroene reaction, but also the  $\cdot\text{CH}_2\text{SiMe}_3$  radicals do not isomerize. Furthermore, there are no longer two abstraction routes; the only abstraction products besides  $\text{Me}_4\text{Si}$  would be 1,3-butadiene and  $\text{Me}_3\text{Si}\cdot$  radicals. Allyltrimethylsilane is the main silicon-containing addition product, being the only product from addition of  $\cdot\text{CH}_2\text{SiMe}_3$  radicals and also the product from the favored terminal addition of  $\text{Me}_3\text{Si}\cdot$  radicals (Table III).

The retroene reaction is more important in the pyrolysis of III and IV than in I, giving rise to the greater thermal lability of these compounds (Table I) and forming propene and the prominent silicon-containing products dimethylvinylsilane and trimethylvinylsilane, respectively (Table II). Ethene results from both homolysis and radical addition. Hydrogen abstraction from III, as from I, leads to an endo-cyclization product.

The effect of added methyl chloride on product composition is consistent with the foregoing ideas. The methathesis reaction between organosilyl radicals and methyl

chloride essentially converts the former into methyl radicals; accordingly, products attributable to methyl radical reactions increased, while those attributable to organosilyl radical reactions decreased. In the pyrolysis of III and IV, formation of dimethylvinylsilane and trimethylvinylsilane was unaffected, confirming that these are products of retroene reactions (Scheme I).

### Experimental Section

Compounds I-IV were generous gifts from Professor T. J. Barton of Iowa State University, who also gave us calibration samples of the vinylsilanes and the dimethylsilacyclohexene; the dimethylsilacyclopentene was a gift from Dr. G. Manuel of the University Paul Sabatier, Toulouse, France. Other silicon compounds were obtained commercially, as were the hydrocarbons.

Gas kinetic experiments were carried out in the improved LPP and SFR apparatus, as previously described.<sup>13</sup> Most of the SFR measurements were made with a 1.5-m column packed with 80-100 mesh Chromosorb 101 with a flow rate of  $60\text{ cm}^3\text{ min}^{-1}$ , temperature programmed between 50 and 210 °C; a 2.5-m column packed with 10% SE-30 on 100-120 mesh diatomite was also used for some of the least volatile products. Retention times are listed in Table II. The same columns were used in the static pyrolysis apparatus attached to a GC/mass spectrometer, on which identification of every product was verified.

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**Registry No.** I, 18163-02-5; II, 763-13-3; III, 33932-65-9; IV, 763-21-3;  $\text{C}_2\text{H}_4$ , 74-85-1;  $\text{C}_3\text{H}_6$ , 115-07-1;  $\text{C}_4\text{H}_8$ , 106-98-9;  $\text{Me}_3\text{SiH}$ , 993-07-7;  $\text{Me}_4\text{Si}$ , 75-76-3;  $\text{HMe}_2\text{SiCH}_2\text{CH}_2$ , 18243-27-1;  $\text{Me}_3\text{SiCH}_2\text{CH}_2$ , 754-05-2;  $\text{HMe}_2\text{CH}_2\text{CH}_2\text{CH}_2$ , 3937-30-2;  $\text{Me}_3\text{SiCH}_2\text{CH}_2\text{CH}_2$ , 762-72-1.

(13) Davidson, I. M. T.; Dean, C. E. *Organometallics*, in press.

## Steric and Electronic Factors Influencing Transition-Metal-Phosphorus(III) Bonding<sup>1</sup>

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Literature data for the heats of reaction of phosphorus(III) compounds with  $(\eta\text{-C}_5\text{H}_7\text{NiMe})_2$ ,  $\text{MePt}(\text{PPhMe}_2)_2(\text{THF})^+$ , and  $\eta\text{-CH}_3\text{C}_6\text{H}_5\text{Mo}(\text{CO})_3$  have been quantified in terms of  $\sigma$ -electronic ( $pK_a$  values of  $\text{R}_3\text{PH}^+$ ),  $\pi$ -electronic ( $E_{\pi a}$  values), and steric (cone angle,  $\theta$ ) properties of the ligands. The heats of reaction are linear functions of  $pK_a$ ,  $E_{\pi a}$  (after the  $\pi$ -electronic threshold,  $\pi_t$ ), and  $\theta$  (after the steric threshold).  $\pi_t$  is a metal property and provides a ranking of the valence orbital energies of the various metals. Steric effects are important for all the reported heats of reaction for the formation of the octahedral complexes  $\text{L}_3\text{Mo}(\text{CO})_3$  but are not important for  $\eta\text{-C}_5\text{H}_7\text{Ni}(\text{Me})\text{L}$ . The formation of  $\text{MePt}(\text{PPhMe}_2)_2\text{L}^+$  exhibits steric effects only for the larger class II and class III ligands. Steric factors are more important for the class III ( $\pi$ -acid) ligands, which show a smaller steric threshold, than for the class II ( $\sigma$ -donor) ligands. The extension of these concepts to the dissociation of CO from *mer*-(CO)<sub>3</sub>LRu(SiCl<sub>3</sub>)<sub>2</sub> shows that steric acceleration of this reaction, which occurs in two narrow regions (steric windows), is determined by a combination of ground-state and transition-state steric effects.

### Introduction

The development of a detailed understanding of the transition-metal-phosphorus bond is a problem that has

been attacked by an impressive arsenal of techniques including theoretical calculations,<sup>2,3</sup> IR,<sup>2c,d,4</sup> NMR,<sup>5</sup>

(1) Second in a series of papers on the Quantitative Analysis of Ligand Effects (QALE). Previous paper: Golovin, M. N.; Rahman, Md. M.; Belmonte, J. E.; Giering, W. P. *Organometallics* 1985, 4, 1981-91.

(2) (a) Marynick, D. S. *J. Am. Chem. Soc.* 1984, 106, 4064-65. (b) Whango, M. H.; Steward, K. R. *Inorg. Chem.* 1982, 21, 1720-1. (c) Xiaoxo, S.; Trogler, W. C.; Ellis, D. C.; Berkovitch-Yellin, Z. *J. Am. Chem. Soc.* 1983, 105, 7033-37.